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LETTER TO THE EDITOR

Shape-resonance-induced non-Franck–Condon vibrational intensities in $3\sigma_g$ photoionisation of N_2†

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Abstract. We report a broad pattern of non-Franck–Condon vibrational intensities extending over about 25 eV of the $3\sigma_g$ photoionisation continuum of N_2. The effect was recently predicted theoretically to arise from shape-resonance-enhanced coupling between electronic and nuclear motion. Here experiment and theory are compared directly for the first time. Qualitative agreement verifies the basic theoretical concept, yet significant quantitative differences indicate the need for further work.

Recently, Dehmer *et al* (1979, referred to hereafter as DDW) showed that shape resonances in molecular photoionisation will couple with vibrational motion, leading to a breakdown in the Franck–Condon separation of electronic and vibrational modes. Using the $3\sigma_g$ channel of N_2 as an example, DDW showed that the σ_u shape resonance at about 13 eV kinetic energy exhibits substantial changes in resonance position and width as a function of (fixed) internuclear separation R. This, in turn, produces different resonance parameters for alternative vibrational channels since the respective Franck–Condon (FC) overlap integrals preferentially weight different regions of R. The result is a significant deviation of the vibrational branching ratios relative to the FC factors over a substantial energy range, which can be many times larger than the net (vibrationally unresolved) resonance half-width. This picture was verified experimentally by Stockbauer *et al* (1979) for the analogous 5σ photoionisation channel in CO. Although the CO experiment unequivocally demonstrated the shape-resonance effects in the vibrational branching ratios at the qualitative level, several quantitative questions remain which can only be answered by a direct comparison between experimental and theoretical results on the same system. For instance, how well do the DDW calculations give the absolute magnitude and positions of maxima and minima in the oscillatory pattern exhibited by the vibrational branching ratios? To address this issue, we report here the $(v = 1)/(v = 0)$ vibrational branching ratio for the $3\sigma_g$ photoionisation channel of N_2.

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The instrument used in this work is described in detail elsewhere (Parr *et al* 1979) and is only summarised briefly here. The new high-flux, two-metre, normal-incidence monochromator (Ederer *et al* 1979) at the Synchrotron Ultraviolet Radiation Facility (SURF-II) of the National Bureau of Standards was used for these measurements. This monochromator provides approximately 10^{10} photons s^{-1} $Å^{-1}$ per milliamp of circulating current (typical initial current ~10 mA) at 1000 Å and provides sufficient radiation for the present measurements down to about 325 Å. The high flux is obtained by accepting about 65 mrad of the synchrotron radiation and by utilising the small vertical dimension (~80 μm) of the stored electron beam as the entrance aperture of the monochromator. Together with 1200 lines/mm grating and a 200 μm exit slit, this configuration yields a photon resolution of about 0·8 Å. The dispersed light is channelled by a 2 mm internal diameter capillary tube for a distance of 25 cm to the interaction region of the experimental chamber. The electron energy analyser is a rotatable, 2 in mean-radius, hemispherical device described elsewhere (Dehmer and Dill 1978). It was operated at a constant resolution of about 100 meV full width at half maximum in these experiments. The light is horizontally polarised and, accordingly, the analyser rotates in a plane perpendicular to the propagation direction of the light, measuring a differential cross section given by

$$d\sigma/d\Omega = (\sigma/4\pi)[1 + \tfrac{1}{4}\beta(3P\cos(2\theta) + 1)]$$

where σ is the integrated photoionisation cross section, P is the polarisation of the light, β is the asymmetry parameter and θ is the angle between the ejected electron and the electric vector. As we are concerned with relative measurements in this work, the analyser was set at an observation angle chosen to eliminate the β-dependent term in $d\sigma/d\Omega$. A 'magic' angle $\theta = 64°$ was chosen based on a polarisation P of about 0·6. A later, more accurate determination of the light polarisation yielded $P \sim 0{\cdot}75$, requiring an observation angle $\theta = 58°$ (just outside the analyser acceptance angle of $\pm 4°$) in order to eliminate totally angular distribution effects. The resulting error can be estimated by theoretical (DDW) and experimental results (Mintz and Kuppermann 1978 and references therein) on the v-dependent β for this process, and is found to result in shifts between 0 and +5% in the reported branching ratios, i.e., within the present error bars. Hence, the present results are little affected. More accurate branching ratios will be a byproduct of planned measurements of the photoelectron angular distributions of these vibrational channels.

Branching ratios for the $v = 0, 1$ levels of $N_2^+ X\,{}^2\Sigma_g^+$ are given as a function of photon energy in figure 1. The present data are denoted by full circles with error bars indicative of the precision of the computer fit to the $v = 0, 1$ peaks in the experimental spectrum. The theoretical prediction by DDW is given by the full curve. Other points of reference include the Franck–Condon factor of 9·3% (D L Albritton 1979, private communication), which would apply if nuclear and electronic motion were completely separable and data (▲) in the 16–23 eV region and at 40·8 eV taken by Gardner and Samson (1978) using laboratory line sources.

The central message in figure 1 is that, as predicted by theory (DDW), the vibrational branching ratio exhibits a gross oscillation relative to the Franck–Condon factor over a broad 30 eV spectral range. This verifies, by direct comparison between experiment and theory, that shape resonances invalidate the Franck–Condon separation and that the resulting vibrational effects can extend far beyond the resonance half-width, approximately 5 eV in this case. Several secondary points also stand out in figure 1. First, the branching ratio exhibits a seemingly erratic behaviour in the

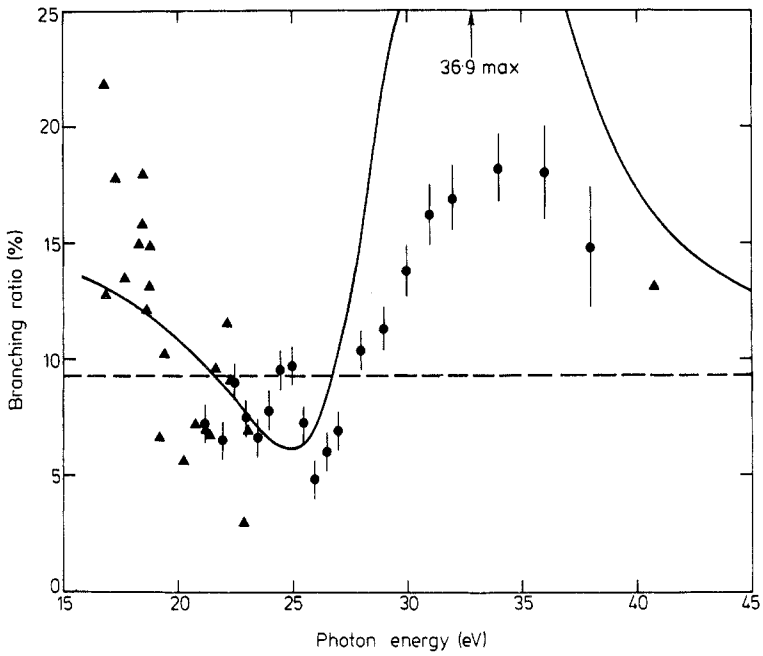

Figure 1. Branching ratios as a function of photon energy for production of the $v = 0, 1$ levels of $N_2^+ X\,^2\Sigma_g^+$ by photoionisation of N_2: ●, present results; ▲, data from Gardner and Samson (1978); —, theory from DDW; ---, the Franck–Condon factor of 9·3% (D L Albritton 1979, private communication).

16–26 eV region with several data points from Gardner and Samson (1978) being out of the frame of figure 1. We attribute this to effects of incompletely resolved autoionising states which are populated in this wavelength range (Gürtler *et al* 1977). In this case, autoionisation effects obscure the mapping of the shape-resonance effect, but are the primary focus of parallel studies performed on a much finer energy mesh. Second, experiment and theory agree rather well in magnitude at the lower and higher energies in figure 1 and in the location of the maxima and minima; however, theoretical results overestimate the branching ratio by about a factor of two at the maximum. Thus, while the qualitative basis for this effect has been firmly established, future work is needed to achieve a quantitative theory. Third, the contrast in branching ratio peak positions in N_2 and CO, noted by Stockbauer *et al* (1979), has been verified. That is, in N_2, the branching ratio peaks several volts above the σ_u resonance position at about 30 eV, whereas in CO the opposite is true (Plummer *et al* 1977, Dehmer *et al* 1979, Stockbauer *et al* 1979). This was tentatively interpreted by Stockbauer *et al* (1979) in terms of the relative positions of the neutral and ionic potential energy curves, i.e., CO contracts slightly and N_2 expands slightly upon removal of an electron from the outermost molecular orbital (Herzberg 1950). Note that this qualitative explanation still awaits theoretical confirmation and should not be extended to other cases without caution, as it does depend on the details of the FC overlap between initial- and final-state vibrational wavefunctions.

We conclude by stressing two points brought out in this work. First, the agreement between theory and experiment indicated here confirms the qualitative aspects of the interpretation by DDW and thus offers support for their speculation that similar

vibrational effects may be expected in conjunction with the widespread occurrence of shape resonances in the inner- and outer-shell spectra of molecules (DDW and references therein). Of course, much more extensive mapping of these effects is needed to test the limits of this generalisation. The second point concerns the implications of the quantitative differences between experiment and theory. These differences could arise from the use of the multiple-scattering model (Dill and Dehmer 1974, Dehmer and Dill 1979), which is designed to give a realistic, though not necessarily highly accurate, representation of molecular photoionisation. They could also arise simply from the use of an independent-electron model, as experience in atomic physics (see, e.g., Starace 1979) indicates that shape-resonance effects are overestimated in one-electron treatments. This, then, would apply even when more accurate independent-electron treatments are used. This is probably a significant part of the problem, and its solution would require the introduction of electron correlations into the theory. Less likely sources of the problem would be nonadiabatic nuclear motion effects and the use of harmonic-oscillator vibrational functions by DDW. In any case, the present work provides a basis for judging future improvements in the theory.

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